

## NO DRAWINGS

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(54) PROCESS FOR THE MANUFACTURE OF  
 ORGANIC ISOCYANATES

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to the manufacture of isocyanates by the reaction of compounds containing aliphatically bound halogen atoms and inorganic cyanates.

15 It is known that organic isocyanates can be obtained from organic halides, particularly those in which the halide is attached to an aliphatic carbon atom, by reaction with alkali metal, alkaline earth metal or ammonium cyanates at elevated temperatures. It is also known that side reactions such as polymerisation of the isocyanate group to give polymers having an isocyanurate ring structure and formation of polyurets by reaction of isocyanate with minor impurities containing isocyanate-reactive hydrogen atoms take place both during the reaction and in the working-up or isolation of the product and lead to reduction in yield of the desired product. It has now been found that the loss in yield occurring on isolation can be considerably reduced by having a small amount of acid present in the reaction mixture during isolation of the product.

35 Thus according to the present invention there is provided a process for the manufacture of organic isocyanates comprising reacting an organic halide containing at least one aliphatically bound halogen atom as herein-after defined with an alkali metal, ammonium or ethyl or methyl substituted ammonium or alkaline earth metal cyanate characterised in

that a small amount of acid is present during isolation of the product.

Although it is a feature of this invention that a small amount of acid be present during the isolation of the product the time or point of addition of the acid may be varied considerably. For example the acid may conveniently be added after removal of inorganic salts by filtration, alternatively it may be added before such a filtration stage, during the reaction itself, or alternatively mixed with the reactants at the beginning of the reaction.

Acids which may be used in the process of the present invention include in particular mineral acids and organic sulphonic acids, for example, meta-phosphoric acid, orthophosphoric acid, p-toluene sulphonic acid, methane sulphonic acid, sulphuric acid, hydrogen chloride and fluoboric acid.

The amount of acid which may be used in the present process is comparatively small compared to the amounts of the reactants, amounts from 0.1 % to 10 % by weight of the organic halide have been found to be convenient although amounts outside these limits may be useful.

Organic halides which can be used in this process are those in which there is at least one halogen atom which is aliphatically bound; by the term aliphatically bound is intended direct attachment of the halogen atom to a saturated aliphatic carbon atom as distinct from a carbon atom in an aromatic or an unsaturated heterocyclic ring. The term aliphatic carbon atom includes carbon atoms in cycloaliphatic rings.

Organic halides to which the process can be applied include alkyl halides, cycloalkyl halides, halogenated aliphatic ethers, halogenoalkylarenes, halogenoalkyl aryl ethers,

(19)



alkenyl halides, halogenoesters and halogeno-ketones.

- Examples of individual organic halides which can be used include methyl iodide, ethyl bromide, isopropyl chloride, tertiary butyl chloride, *n*-butyl bromide, *n*-hexyl bromide, cyclohexyl bromide, hexamethylene dibromide, 1,4-dibromocyclohexane, decyl bromide, decamethylene dibromide, dodecyl chloride, *n*-octadecyl bromide, allyl chloride; 1,4 - dichlorobut - 2 - ene; 1,3 - chlorobromo - propane, products obtained by chloromethylation of alcohols and mixtures thereof, for example, methoxymethyl chloride, ethoxymethyl chloride, 2-chloroethoxymethyl chloride, 2 - ethoxy - ethoxymethyl chloride, *n*-butoxymethyl chloride, cyclohexyloxymethyl chloride, ethylene glycol bis - (chloromethyl) ether, 1,2-propylene glycol bis-(chloromethyl) ether, 1,3-propylene glycol bis-(chloromethyl) ether, 1,4-tetramethylene glycol bis-(chloromethyl) ether, diethylene glycol bis-(chloromethyl) ether, dipropylene glycol bis-(chloromethyl) ether, 1,1,1 - trimethylol - propane tris-(chloromethyl) ether, allyl chloromethyl ether, benzyl chloromethyl ether,  $\beta$ -phenylethylchloromethyl ether,  $\beta$ -phenoxyethyl chloromethyl ether, *p*-xylylene diol bis-(chloromethyl) ether and 1,4 - bis(2' - chloromethoxy ethoxy)benzene; 2-chlorotetrahydrofuran, monochlorodioxan,  $\alpha$ -chloroethylmethylether, 1,2 - dimethoxy - 1,3 - dichloroethane, ethyl chloroacetate, ethyl  $\beta$ -chloropropionate, tris-(chloroethyl)phosphate, tris - ( $\beta$  - bromopropyl)phosphite, bis - (chloroethyl)phthalate; compounds obtained by chloromethylation of aromatic hydrocarbons and ethers, for example, benzyl chloride, 2-, 3- and 4- methyl benzyl chlorides, 2-, 3- and 4-ethyl benzyl chlorides, 2,4-dimethyl benzyl chloride, 2,4,6-trimethyl benzyl chloride, *m*-xylylene dichloride, *p*-xylylene dichloride, 4,6 - dimethyl - *m* - xylylene dichloride, 2,4 - bis - (chloromethyl)toluene, 2,4 - bis - (chloromethyl) - *p* - xylene, bis-(chloromethyl)mesitylene, bis-(chloromethyl)pseudocumene, bis-(chloromethyl)hemimellitene, bis - (chloromethyl) - durene, bis-(chloromethyl)isodurene, tris-(chloromethyl)toluene, tris-(chloromethyl)ethyl benzene, tris - (chloromethyl) - *m* - xylene and tris-(chloromethyl)mesitylene,  $\alpha$ -naphthylmethyl chloride,  $\beta$ -naphthylmethyl chloride, 2,6-bis(chloromethyl) naphthalene,  $\alpha$ -chloromethyl tetralin,  $\beta$ -chloromethyl tetralin, 1,3 - bis - (chloromethyl)tetralin, 9,10 - bis - (chloromethyl)anthracene, 9,10 - bis - (chloromethyl) - 1,2,3,4,5,6,7,8 - octahydroanthracene, 4-chloromethyl diphenyl, 4,4' - bis - (chloromethyl) - diphenyl, 2,4,4' - tris - (chloromethyl)diphenyl and related products obtained by chloromethylation of diphenyl alkanes, diphenyl ether, diphenylsulphide, diphenylsulphone and diphenoxyalkanes, 4-methyl benzyl chloride, 4-ethoxybenzyl chloride, 2,4 - bis - (chloromethyl)

anisole, 2,4 - bis - (chloromethyl) - 3,5 - dimethyl anisole, 2,4,6 - tris - (chloromethyl) - 3,5 - dimethyl anisole, 4-chlorobenzyl chloride, 3,4-dichlorobenzyl chloride, bis - (chloromethyl) - monochlorobenzene, 2 - chloromethyl - 4 - chlorotoluene, 2,6 - bis - (chloromethyl) - 4 - chlorotoluene, 2 - chloromethyl - 4 - bromoethyl benzene and related chloromethylates of halogenated alkylated benzenes, 1 - chloro - 1 - phenyl ethane, 1 - chloro - 2 - (4' - chlorophenyl)ethane, 1 - chloro - 2 - (2' - chlorophenoxy)ethane, 2,2'-dichlorodiethyl ether, 1 - (4' - chloromethylphenoxy) - 2 - chloroethane, 3-nitrobenzylchloride, 3 - nitro - 4 - methyl - benzyl chloride, bis - (chloromethyl) - *m* - chloro - anisole, 3-chloroethyl acetophenone and 3,3' - bis(chloromethyl) - benzophenone.

Mixtures of products particularly those obtained by the chloromethylation of aromatic hydrocarbons may be used, such starting materials are particularly useful for obtaining liquid isocyanate mixtures.

The process of the present invention is particularly applicable to the manufacture of isocyanates from  $\alpha$ -haloalkylarenes containing one or more  $\alpha$ -haloalkyl radicals attached to an aromatic nucleus, in particular compounds obtained by the chloromethylation of benzene or an alkyl substituted benzene.

Alkali metal, alkaline earth metal on ammonium cyanates which may be used in the present process include the cyanates of lithium, sodium, potassium, magnesium, calcium, strontium, barium, and the ammonium ion. They also include the cyanates of substituted ammonium ions such as methyl ammonium, dimethylammonium, trimethylammonium and triethylammonium cyanates.

It is desirable to use a solvent preferably one in which the cyanate is soluble to some extent; the solubility of metal cyanates in organic solvents is however known to be low and it is desirable that the cyanate be introduced in a finely divided form.

Examples of solvents which may be used include tertiary amides such as dimethyl formamide, sulfoxides such as dimethylsulphoxide, sulphones such as diphenylsulphone, nitriles such as acetonitrile and benzonitrile, ketones such as acetone, methyl ethyl ketone, cyclohexanone and methyl isobutyl ketone, methyl - *N,N* - dimethyl carbamate, ethyl - *N,N* - dimethyl carbamate, *N*-carbethoxy piperidine, *n*-butyl acetate, propyl acetate, ethylene and propylene carbonates, ethylene glycol dimethyl ether and 2-methoxy ethyl acetate and esters of phosphonic acids such as the dimethyl ester of methyl phosphonic acid. Mixtures of solvents may be used.

There may be used as solvents mixtures of polar solvents with hydrocarbons or halogenated aromatic hydrocarbons. Polar solvents which may be used in such mixtures include amides, carbamates, sulphones, ureas, nitriles,

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5 -		nitro compounds and phosphonamides, for	is employed for each aliphatically bound
yl) -		example, dimethylformamide, N-methyl	halogen atom in the starting material and
nzyl		pyrrolidone, formamide, acetamide, N-methyl	the cyanate is preferably employed in excess.
is -		acetamide, diethyl formamide, diisopropyl	The amount of catalyst used may be from
2 -	70	formamide, diphenyl formamide, methyl ethyl	0.001 % to 5 % by weight of the organic
is -		formamide, methyl ethyl acetamide, dicyclo-	halide although amounts outside this range
oro-		hexyl acetamide, ethyl cyclohexyl acetamide,	may be used if desired.
ated		ethyl phenyl acetamide, N - isopropyl -	At the completion of the heating period,
ben-		pyrrolidone, N-methyl piperidone, N-methyl	it is desirable to remove inorganic material
1 -	75	caprolactam, ethyl N,N-dimethyl carbamate,	by filtration before isolation of the product
1 -		methyl N,N-diethyl carbamate, N-carbometh-	by distillation. If not previously added the
ane,		oxy piperidine, dimethyl sulphone, tetra-	acid must be added after the filtration before
oro-		methylene sulphone, pentamethylene sulphone,	any distillation takes place, the acid may
tro-		methyl ethyl sulphone, methyl cyclohexyl sul-	however be added earlier in the process, for
nzyl	80	phone, methyl benzyl sulphone, methyl phenyl	example at the end of the reaction before
ro -		sulphone, diphenyl sulphone, tetramethyl urea,	filtration, during the reaction at elevated tem-
3' -		hexamethyl phosphonamide, acetonitrile, pro-	perature or during the initial mixing of the
		pionitrile, benzonitrile, 3 - methoxy - propio-	reactants prior to heating.
hose		nitrile, cyclohexane nitrile, benzyl cyanide,	The process may be used for the manu-
natic	85	succinonitrile, adiponitrile, nitrobenzene, the	facture of monoisocyanates or for isocyanates
ting		nitrotoluenes, nitromethane, nitroethane and	containing two or more isocyanate groups.
ain-		nitropropane.	Such isocyanates may be used for the manu-
		Solvents of low polarity which may be used	facture of monomeric, oligomeric or polymeric
n is		in such mixtures include aliphatic, cycloali-	urethanes or ureas by known processes.
e of	90	phatic, aromatic and araliphatic hydrocarbons	The invention is illustrated but not limited
tain-		such as benzene, toluene, xylene, diethyl ben-	by the following examples in which all parts
ched		zene, isopropyl benzene, ethyl naphthalene,	and percentages are by weight except where
com-		octane, petroleum ethers, cyclohexane and	otherwise stated.
n of		methyl cyclohexane, halogenated aromatic	Example 1
	95	hydrocarbons such as monochlorobenzene, the	A mixture of 11.6 parts of bis(chlormethyl)
on		dichlorobenzenes, trichlorobenzene.	durene, 7.3 parts of sodium cyanate, 55 parts
n the		The use of mixtures of solvents of high	of monochlorobenzene, 50 parts of N,N-
ium,		and low polarity in this section is the sub-	dimethyl acetamide and 0.4 parts of iodine
ium,		ject of our copending application No.	was stirred at between 110°C. and 130°C.
ion.	100	31891/69, (Serial No. 1316951). Which also	for 40 minutes. The hot reaction mixture was
uted		claims α-isocyanatoalkyl mesitylenes contain-	filtered and to the filtrate was added 0.24
ium,		ing 1, 2 or 3 α-isocyanatoalkyl groups.	parts of p-toluene sulphonic acid. Evaporation
and		The present process may be carried out in	of the filtrate to dryness gave 11.6 parts of
ably	105	the presence of known catalysts for the reac-	solid residue from which 6.4 parts of bis
ome		tion, including for example copper and its	(isocyanatomethyl)durene were obtained by
s in		salts, quaternary ammonium salts, particularly	crystallisation.
low		bromide and iodide, and iodides of alkali and	Example 2
tro-		alkaline earth metals.	The foregoing reaction was modified by
	110	The process may also be carried out using	addition of 0.2 parts of metaphosphoric acid
used		iodine, bromine, iodine chlorides or mixtures	to the reactants and omission of p-toluene
orm-	45	thereof as catalyst. The use of such catalysts	sulphonic acid from the working-up procedure.
isul-		is the subject after of our copending Appli-	6.7 Parts of bis(isocyanatomethyl)durene were
one,		cation No. 31892/69. (Serial No. 1316952).	thereby obtained.
rile,	115	As iodine chlorides there may be men-	Example 3
one,		tioned the monochloride and the trichloride.	The reaction performed in Example 1 was
yl -		Iodine and iodine monochloride are pre-	repeated with addition of 0.2 parts of meta-
oxy		ferred catalysts.	phosphoric acid immediately prior to filtra-
ate,	120	The reaction is normally carried out at	tion. The filtrates were evaporated to dryness
lene		atmospheric pressure at temperatures of from	and crystallisation of the resulting residue
thyl	55	20°C to 250°C although temperatures out-	give 7.0 parts of bis(isocyanatomethyl)durene.
such		side this range can be used. A preferred	A similar preparation to the above when
onic		reaction temperature is from 50°C to 160°C.	carried out without acid addition gave poly-
	125	The process is carried out by heating together	meric material devoid of isocyanate groups
s of		the halide and cyanate optionally in the pre-	on examination by infra-red spectroscopy.
gen-	60	sence of a catalyst and preferably in the pre-	Example 4
ents		sence of a solvent; the period of heat-	A mixture of 11.6 parts of bis(chloromethyl)
ude		ing required is to a large extent dependent	durene, 7.3 parts of sodium cyanate, 50 parts
iles,	130	on the halide used, on the temperature and on	(by volume) of monochlorobenzene, 50 parts
		the catalyst employed.	
	65	At least one molar proportion of the cyanate	

(by volume) of N,N-dimethylacetamide and 1 part of iodine trichloride were stirred at the reflux under nitrogen atmosphere. After 15 minutes reaction was complete as determined by vapour phase chromatography (V.P.C.) examination. After filtration at 80°C, the filtrates were treated with 0.2 parts of metaphosphoric acid and evaporated to dryness yielding 14.0 parts of crude bis(isocyanatomethyl)urene.

#### Example 5

A mixture of 4.0 parts of ethylene glycol bis(chloromethyl)ether, 5.0 parts of potassium

cyanate 47.5 parts (by volume) of monochlorobenzene, 2.5 parts (by volume) of N,N-dimethylacetamide, 0.15 parts of iodine and 0.15 parts of meta-phosphoric acid were stirred at the reflux. A similar preparation with the omission of iodine and acid was performed. Samples from both preparations at various time intervals were cooled, centrifuged and the decanted liquors examined by Infra-red spectroscopy using 0.1 mm path length matched sodium chloride solution cells. Optical density measurements of the isocyanate peak at 2260  $\text{cm}^{-1}$  were made and are given in the following table.

TABLE  
NCO peak at 2260  $\text{cm}^{-1}$  Optical density measurements

Time	Sample	Optical density measurements	
		Iodine— $\text{HPO}_3$	No iodine or phosphoric acid
0	0	0	0
37 mins	1	0.54	0.19
55 mins	2	0.34	0.25
78 mins	3	0.37	0.24
169 mins	4	0.29	0.23

The higher figure for the optical density of the isocyanate peak indicates the advantage of using a combination of iodine and phosphoric acid.

#### WHAT WE CLAIM IS:—

1. A process for the manufacture of organic isocyanates comprising reacting an organic halide containing at least one aliphatically bound halogen atom as hereinbefore defined with an alkali metal, ammonium or methyl or ethyl substituted ammonium or alkaline earth metal cyanate characterised in that a small amount of acid is present during isolation of the product.

2. A process as claimed in Claim 1 wherein the acid is a mineral acid or an organic sulphonic acid.

3. A process as claimed in Claim 1 or Claim 2 wherein the acid is mixed with the reactants at the beginning of the reaction.

4. A process as claimed in any of the preceding claims wherein the amount of acid is from 0.1 % to 10 % by weight of the organic halide.

5. A process as claimed in any of the pre-

ceding claims wherein the organic halide is an  $\alpha$ -haloalkylarene containing one or more  $\alpha$ -haloalkyl radicals attached to an aromatic nucleus.

6. A process as claimed in Claim 5 wherein the  $\alpha$ -haloalkylarene is a compound obtained by chloromethylation of benzene or an alkyl substituted benzene.

7. A process as claimed in any of the preceding claims wherein a catalyst is used.

8. A process as claimed in Claim 7 wherein the catalyst is iodine, iodine monochloride or a mixture thereof.

9. A process as claimed in any of the preceding claims wherein the reactants are heated at a temperature within the range 50°C to 160°C.

10. A process according to Claim 1 as hereinbefore described with reference to the examples.

11. Organic isocyanates whenever manufactured by a process as claimed in any of the preceding claims.

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